**IN THE UNITED STATES PATENT**

**AND TRADEMARK OFFICE**

Applicant(s): Yasuyuki Mizuno et al
Serial No.: 10/529,738
Filed: March 30, 2005
For: RESIN COMPOSITION FOR PRINTED WIRING BOARD AND VARNISH, PREPREG AND METAL CLAD LAMINATED BOARD USING THE SAME
Art Unit: 1796
Examiner: Robert E. Sellers

Honorable Commissioner of Patents
and Trademarks
Washington, D.C. 20231

**DECLARATION UNDER 37 CFR 1.132**

SIR:

I. I, Yasuyuki Mizuno, a first inventor of this case, declare and say as follows.

I got a Bachelor degree in engineering from Shinshu University in 1991, and entered Hitachi Chemical Company, Limited in April 1991. I have made researches in resin materials and substrates for printed wiring boards in Hitachi Chemical Company, Limited since September 1993. I studied the Official Action dated January 16, 2009 received in the parent application of said application.

In order to show that the present invention has the effects in the claimed range of biphenyl structure-containing epoxy resin, I have conducted additional experiments as mentioned below under my supervision.

II. Additional experiments

The additional experiments show good effects of the present composition in the claimed range of biphenyl structure-containing epoxy resin, whereas poor effects with composition out of the claimed range.

EXPERIMENT

(1) Sample

Resin varnishes (EX-1 to 14) are prepared according to the formulation amount as shown in Table 1-1 and 1-2. In each varnish, polyphenylene ether resin is formulated in an amount of 30 parts by weight based on the total amount of 100 parts by weight of cyanate ester compound and biphenyl skeleton type epoxy resin.

(a) Varnishes

**EX-1**

In a 1-liter four-nekced separable flask equipped with a thermometer, a condenser and a stirring device, 85g of toluene, polyphenylene ether resin (PKN 4752, available from Japan GE) were charged, and the mixture was heated to 90°C and dissolved under stirring. Then, 148g of 2,2-bis(4-cyanatophenyl)propane (BADCY, available from Lonza) and 4.5g of p-(α-cumyl)phenol (available from Tokyo Kasei Kogyo Co., Ltd.) were charged, after confirmation of dissolution, the mixture temperature was maintained at 110 °C, then 0.049g of Manganese naphthenate (available from Wako Pure Chemical Industries, Ltd.) as reaction promoter was formulated, to heat react for about three hours, obtaining phenol modified cyanate ester oligomer solution which is compatible with polyphenylene ether resin.

Next, this solution is cooled. When the solution temperature becomes 80 °C, 95g of methylethylketone, 7.4g of

3,3′,5,5′-tetramethylbiphenol diglycidyl ether (YX-4000, available from Japan Epoxy Resin Co.) as biphenyl type epoxy resin are formulated while stirring. After confirmation of dissolution, it was cooled to room temperature, then 13.6g of p-(α-cumyl)phenol and 0.018g of zinc naphthenate (Wako Pure Chemical Industries, Ltd.) as curing promoter are formulated to prepare resin varnish having a non-volatile concentration of about 55 % by weight.

**EX-2～9**

A resin varnish having a non-volatile concentration of about 55 % by weight was prepared in analogous to the procedure of EX-1 except that the formulation was changed to the amount shown in Table 1-1 and 1-2 in the above EX-1 formulation.

**EX-10**

A resin varnish having a non-volatile concentration of about 55 % by weight was prepared in analogous to the procedure of EX-1 except that biphenyl aralkylene novolak epoxy resin (NC-3000H, available from Nippon Kayaku Co., Ltd.) is used instead of YX-4000 as biphenyl type epoxy resin.

**EX-11～14**

A resin varnish having a non-volatile concentration of about 55 % by weight was prepared in analogous to the procedure of EX-10 except that the formulation was changed to the amount shown in Table 1-2 in the above EX-10 formulation.

(b) Prepreg

(Preparation of prepreg)

The resin varnishes obtained in EX-1 to 14 were each impregnated into a glass cloth (E glass) with a thickness of 0.15 mm, and made through a gap of about 0.35mm. Then, the material was dried at 160°C for 4 to 7 minutes to obtain the respective prepregs with a resin solid content of 52% by

weight.

(c) Copper clad laminated board

(Preparation of copper clad laminated board)

Four sheets of the above obtained prepregs were laminated, and copper foils with a thickness of each 18 μm were provided on the both outermost layers, and molding was carried out under the pressing conditions of 230°C for 70 minutes and 2.5MPa by heating and pressure to prepare a both-surface copper clad laminated board.

(2) Evaluation method

(Evaluation methods of the characteristics of the copper clad laminated board)

With regard to the obtained copper clad laminated board, copper foil peeling strength, dielectric characteristics, solder heat resistance, water absorption rate, thermal expansion coefficient (α), Tg (glass transition temperature) and bending characteristics were evaluated. The evaluation results are shown in Table 1-1 and 1-2.

Evaluation methods of the characteristics of the copper clad laminated boards are as shown below.

Solder heat resistance of the copper clad laminated boards was examined by first etching the whole surface-copper foil (whole surface-copper foil etched product), and maintain in a pressure cooker tester (conditions: 121°C, 2.0 atm) for 2 hours, then, immersing in a molten solder at 288°C for 20 seconds, and the appearance thereof was judged with naked eyes. The number of test is n=3, in Table, ○ mean as no abnormality, × mean as occurrence of measling or blister.

Thermal expansion coefficient (α) and Tg of the copper clad laminated boards (whole surface-copper foil etched product) were measured by TMA.

Dielectric properties such as dielectric constant (εr) and dielectric dissipation factor (tan δ) of the copper clad laminated boards were measured by a triplate structure line

resonator method using a vector type network analyzer (IPC standard: IPC-TM650, 2.5.5.5.1). Incidentally, the measurement conditions are: frequency: 1 GHz, measurement temperatures: room temperature (25°C).

Water absorption rate of the copper clad laminated boards (whole surface-copper foil etched product) was calculated from a weight difference between the normal state and after maintaining in a pressure cooker tester (conditions: 121°C, 2 atm) for 5 hours (unit: % by weight).

Bending characteristics were obtained by measuring bending modulus at room temperature according to copper clad laminated boards test standard JIS-C-6481, breaking strength and breaking elongation at room temperature.

(3) Results

The formulation and evaluation results are shown in the following Table 1-1 and 1-2.

Table 1-1 Formulation of Varnishes and property evaluation results of laminated board (cont.)

| Item | | | EX-1 | EX-2 | EX-3 | EX-4 | EX-5 | EX-6 | EX-7 |
|---|---|---|---|---|---|---|---|---|---|
| | Biphenyl type Epoxy resin/ Cyanate compound | | 5/100 | 10/100 | 30/100 | 60/100 | 100/100 | 200/100 | 250/100 |
| | PPE(parts by weight, Biphenyl type Epoxy resin + Cyanate compound =100) | | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| Cyanate compound | Bisphenol A type cyanate ester (BADCY) (g) | | 148 | 142 | 121 | 100 | 81 | 55 | 47 |
| Polyphenylene ether resin (g) | | | 47 | 47 | 47 | 48 | 48 | 49 | 49 |
| Epoxy resin | Biphenyl type Epoxy resin (YX-4000) (g) | | 7.4 | 14.2 | 36.4 | 59.9 | 80.8 | 109.4 | 117.7 |
| | Biphenyl type Epoxy resin (NC-3000H) (g) | | – | – | – | – | – | – | – |
| Phenol compound | At reaction of oligomers: p-cumyl phenol (PCP) (g) | | 4.5 | 4.3 | 3.7 | 3.1 | 2.5 | 1.7 | 1.4 |
| | At formulation of varnish: p-cumyl phenol (PCP) (g) | | 13.6 | 13.0 | 11.1 | 9.2 | 7.4 | 5.0 | 4.3 |
| Reaction promoter | Manganese naphtenate (g) | | 0.049 | 0.047 | 0.040 | 0.033 | 0.027 | 0.018 | 0.016 |
| | Zinc naphtenate (g) | | 0.018 | 0.018 | 0.015 | 0.012 | 0.010 | 0.007 | 0.006 |
| Solvent | Toluene (g) | | 85 | 83 | 74 | 65 | 56 | 45 | 42 |
| | MEK (g) | | 95 | 97 | 106 | 115 | 124 | 135 | 138 |
| Varnishes NV(%) | | | 55 | 55 | 55 | 55 | 55 | 55 | 55 |
| Properties of laminated board | Coper foil peeling strength (kN/m) | Normal copper foil (Rz:7 μm) | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.4 | 1.4 |
| | | Low profile copper foil(Rz:3 μm) | 1.1 | 1.1 | 1.1 | 1.0 | 1.1 | 1.0 | 1.0 |
| | εr | 1GHz | 3.48 | 3.47 | 3.49 | 3.50 | 3.51 | 3.54 | 3.62 |
| | tan δ | 1GHz | 0.0050 | 0.0048 | 0.0051 | 0.0052 | 0.0054 | 0.0060 | 0.0063 |
| | Solder hear resistance (288°C) | PCT-1h | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ |
| | | PCT-2h | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ |
| | | PCT-3h | ○○× | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ |
| | | PCT-4h | ××× | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ |
| | | PCT-5h | ××× | ○×× | ○○× | ○○○ | ○○○ | ○○○ | ○○× |
| | Water absorption rate(%) | | 0.52 | 0.51 | 0.50 | 0.55 | 0.54 | 0.56 | 0.63 |
| | TMA | α1(ppm/°C) | 48 | 50 | 52 | 51 | 55 | 52 | 54 |
| | | α2(ppm/°C) | 303 | 282 | 298 | 292 | 278 | 289 | 304 |
| | | Tg(°C) | 191 | 187 | 183 | 185 | 181 | 174 | 171 |
| | Bending properties (R.T.) | Bending modulus(GPa) | 18 | 18 | 18 | 18 | 18 | 18 | 17 |
| | | Breaking strength (MPa) | 478 | 576 | 589 | 611 | 589 | 603 | 573 |
| | | Breaking elongation (%) | 3.2 | 3.6 | 3.7 | 3.8 | 3.7 | 3.8 | 3.7 |

Table 1-2 Formulation of Varnishes and property evaluation results of laminated board

| Item | | | EX-8 | EX-9 | EX-10 | EX-11 | EX-12 | EX-13 | EX-14 |
|---|---|---|---|---|---|---|---|---|---|
| | Biphenyl type Epoxy resin/ Cyanate compound | | 300/100 | 5/100 | 10/100 | 100/100 | 200/100 | 250/100 | 300/100 |
| | PPE(parts by weight, Biphenyl type Epoxy rein + Cyanate compound =100) | | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| Cyanate compound | Bisphenol A type cyanate ester(BADCY) (g) | | 41 | 148 | 142 | 81 | 55 | 47 | 42 |
| Polyphenylene ether resin (g) | | | 50 | 47 | 47 | 48 | 49 | 49 | 50 |
| Epoxy resin | Biphenyl type Epoxy resin(YX-4000) (g) | | 124.0 | – | – | – | – | – | – |
| | Biphenyl type Epoxy resin(NC-3000H) (g) | | – | 7.4 | 14.2 | 80.8 | 109.4 | 117.7 | 124.9 |
| Phenol compound | At reaction of oligomers: p-cumyl phenol (PCP) (g) | | 1.3 | 4.5 | 4.3 | 2.5 | 1.7 | 1.4 | 0.9 |
| | At formulation of varnish: p-cumyl phenol (PCP) (g) | | 3.8 | 13.6 | 13.0 | 7.4 | 5.0 | 4.3 | 2.7 |
| Reaction promotor | Manganese naphtenate (g) | | 0.014 | 0.049 | 0.047 | 0.027 | 0.018 | 0.016 | 0.010 |
| | Zinc naphtenate (g) | | 0.005 | 0.018 | 0.018 | 0.010 | 0.007 | 0.006 | 0.005 |
| Solvent | Toluene (g) | | 40 | 85 | 83 | 56 | 45 | 42 | 40 |
| | Methyl Ethyl Ketone(MEK) (g) | | 140 | 95 | 97 | 124 | 135 | 138 | 140 |
| VarnishsNV(%) | | | 55 | 55 | 55 | 55 | 55 | 55 | 55 |
| Properties of laminated board | Copper foil peeling strength (kN/m) | Normal copper foil (Rz:7 μm) | 1.2 | 1.5 | 1.5 | 1.5 | 1.5 | 1.4 | 1.2 |
| | | Low profile copper foil(Rz:3 μm | 0.7 | 1.1 | 1.1 | 1.0 | 1.0 | 1.0 | 0.8 |
| | εr | 1GHz | 3.78 | 3.50 | 3.49 | 3.53 | 3.58 | 3.67 | 3.81 |
| | tan δ | 1GHz | 0.0077 | 0.0049 | 0.0052 | 0.0055 | 0.0062 | 0.0063 | 0.0074 |
| | Solder heat resistance (288℃) | PCT-1h | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ |
| | | PCT-2h | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ |
| | | PCT-3h | ○○○ | ○×× | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ |
| | | PCT-4h | ○○○ | ××× | ○○○ | ○○○ | ○○○ | ○○○ | ○○○ |
| | | PCT-5h | ○×× | ××× | ○×× | ○×× | ○○× | ○×× | ○○× |
| | Water absorption rate(%) | | 0.71 | 0.48 | 0.49 | 0.52 | 0.55 | 0.63 | 0.69 |
| | TMA | α1(ppm/℃) | 56 | 52 | 50 | 56 | 56 | 54 | 57 |
| | | α2(ppm/℃) | 278 | 293 | 290 | 276 | 280 | 279 | 293 |
| | | Tg(℃) | 163 | 192 | 187 | 181 | 175 | 170 | 159 |
| | Bending properties (R.T.) | Bending modlus(GPa) | 17 | 19 | 18 | 18 | 18 | 17 | 17 |
| | | Breaking strength (MPa) | 503 | 490 | 520 | 584 | 532 | 552 | 504 |
| | | Breaking elongation (%) | 3.4 | 3.1 | 3.5 | 3.7 | 3.8 | 3.6 | 3.0 |

As shown in the above Table, The preferred formulation of biphenyl type epoxy resin according to the present invention is 10 to 250 parts by weight, more preferably 10 to 150 parts by weight, particularly preferably 10 to 100 parts by weight based on 100 parts by weight of cyanate compound. This formulation considered from the balance of humidity resistance of the laminated board, heat resistance at the time of humid conditions, bending strength and elongation, dielectric characteristics at high frequency band region.

As concerns the laminated boards of EX-2 to EX-7 and EX-9 to EX-13 prepared with preferable formulation ratio of biphenyl type epoxy resin and cyanate compound, they gave good values in dielectric constant (εr) at 1 GHz being lower than 3.7, and dielectric dissipation factor (tan δ) being lower than 0.007. These levels of values are applicable to high end applications for high speed and high frequency region. However, EX-8 and EX-14 prepared with higher amount than the preferable range regarding formulation ratio of biphenyl type epoxy resin and cyanate compound, they gave εr over 3.7 and tan δ over 0.007, thereby they are applicable to applications for middle high speed and high frequency region.

Moreover, the laminated boards of EX-2 to EX-7 and EX-9 to EX-13 shows good solder heat resistance under humid conditions, and high bending strength and elongation. On the other hand, EX-1 and EX-9 prepared with less amount than the preferable range regarding formulation ratio of biphenyl type epoxy resin and cyanate compound, they gave poor results in solder heat resistance under humid conditions, bending strength and elongation compared with other laminated boards.

(4) Consideration

In conclusion, the laminated boards of the present invention show well balanced overall performances when prepared with preferable formulation ratio of biphenyl type

epoxy resin and cyanate compound in comparison with the laminated boards prepared out of the said range.

III. Conclusion

I believe that the above results show that present invention has the effects in the claimed range of biphenyl structure-containing epoxy resin.

IV. I further declare that all statements made herein of may own knowledge are true and that all statements made in information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001, of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated: June/10/2009

Yasuyuki Mizuno

Yasuyuki Mizuno